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Nano-Structural Studies of Gel in Super Critical Fluid I -Instrumental Developments-

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In order to investigate nano-structures of gels in super critical fluid by means of a small-angle neutron scattering (SANS) method, an *in situ* observation system has been installed at KUR-SANS spectrometer. In the preliminary experiments, density fluctuation of CO_2 near its critical point was successfully observed with this newly installed system.

Key words : super critical fluid, critical density fluctuation, small-angle neutron scattering

1 INTRODUCTION

Super critical fluid (SCF) is known to exhibit characterizing features both of liquid and gas: high diffusion constant ($\sim 10^{-7}$ $m^2 \cdot s^{-1}$) and high density (~ 500 $kg \cdot m^{-3}$).[1)] These features indicate that the SCF can be a good dissolvent for a lot of useful materials. It is known that the solute and SCF molecules form combined clusters in the mixture.[2)] On the other hand, the pure SCF shows a large density fluctuation near the critical point, indicating emergence of large clusters of SCF molecules.[2)] In the mixture, the emergence of the large SCF-cluster induces destruction of the solute-SCF clusters. Therefore, the solubility of solute shows drastic changes around the critical point through the solute and SCF molecules. These facts suggest that heterogeneous materials composed of the parts with different affinity degree to the SCF, such as block copolymers and heteropolymer gels, can produce nano-structures and exhibit structural transition around critical point.[3)] We have been interested in a heterogeneous structure in gels and its structural transition in the SCF adjacent to the critical point.

Under relatively *mild* conditions (T_c = 304.15 K, P_c = 7.38 MPa), carbon dioxide becomes the SCF, which can dissolve many chemicals. On the other hand, the SCF conditions of water (T_c=647.15 K, P_c=22.06 MPa) are more severe than those of carbon dioxide in spite that the super critical water can decompose most of materials and is useful for processing chemical wastes. From the reasons described above, we have adopted the super critical carbon dioxide as a solvent in the gel.

In order to observe the nano-structures in heterogeneous gels saturated with CO_2-SCF, we utilized a small-angle neutron scattering (SANS) method. Neutron is a suitable probe for investigating the nano-structure of specimens in a high pressure apparatus because it has a high transmission for sapphire glass used for the cell windows.[4)] Therefore, we have installed an *in situ* SANS observation system which can introduce the CO_2-SCF in a neutron beam line.

In the present paper, as the first report of our study, we will describe on the characteristics of our SCF system and the results of observation of the critical phenomena in the

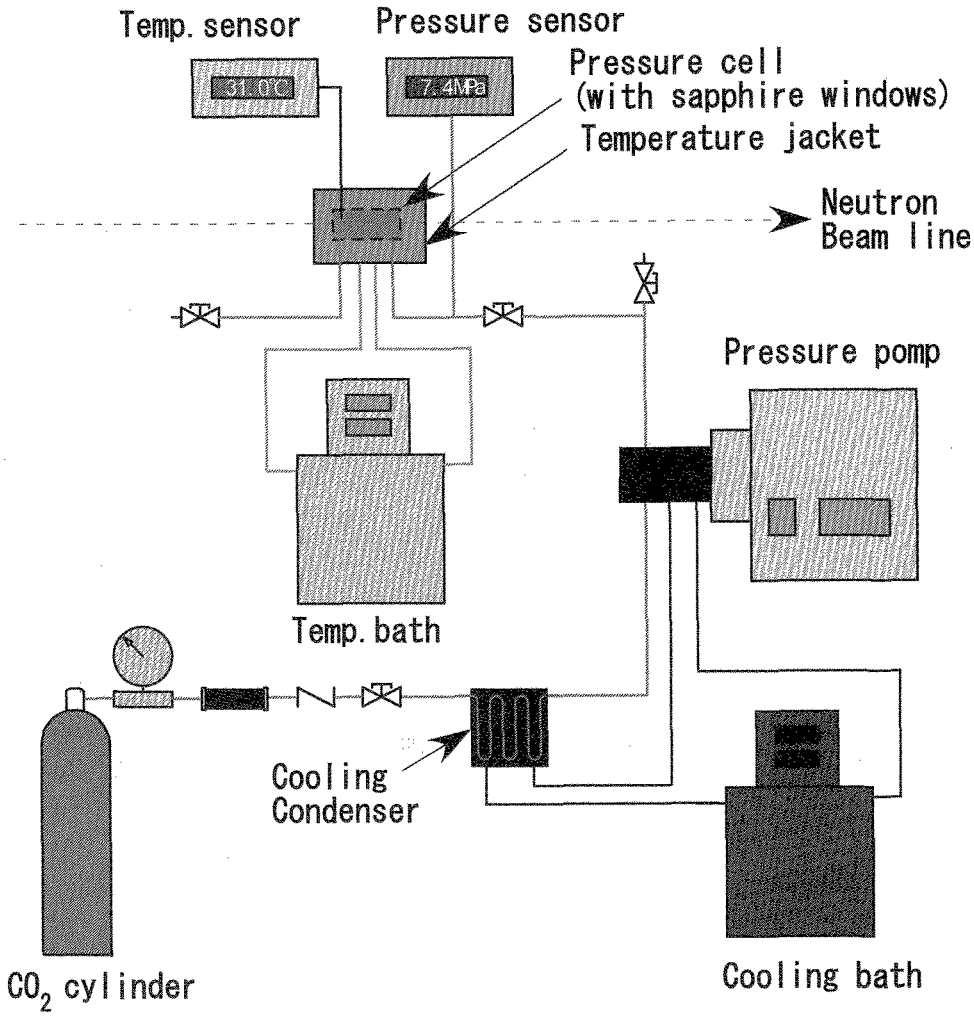

Fig. 1. SCF system for the small-angle neutron scattering experiments at KUR-SANS.

CO_2-SCF, which was carried out for a performance examination of the system.

2 SCF system for SANS apparatus

We installed the *in situ* SANS observation system of the nano-structures in heterogeneous gels saturated with CO_2-SCF at KUR-SANS spectrometer,[5] which is installed at Kyoto University Reactor, Kumatori, Osaka, Japan. As illustrated in Fig. 1, the system is composed of two section: a pressure-generating apparatus and a high pressure cell with optical windows. In the pressure-generating sections, CO_2 becomes liquid by cooling. The liquid CO_2 is compressed and then sent to the optical pressure cell by a pressure pump. The pressure in the cell is controlled by monitoring pressure out of the pump within ± 0.05 MPa. The optical pressure cell is installed in a neutron beam line for *in situ* measurements and has two sapphire widows of which the transmission for neutron is higher than 95 %. The optical length between the windows in the cell can be adjustable in a range of 5-10 mm; the transmission of CO_2-SCF is expected to be 94 % with the optical length of 5 mm. In order to control the temperature of a specimen within $\pm 0.01^\circ$C, the cell is dressed with a jacket in which temperature-controlled water is circulated. The characteristics of optical pressure cell are listed in Table 1.

3 Observation of density fluctuation near critical point

In order to examine the performance of the SCF system, we carried out SANS observations of the nano-structure in the carbon dioxide near the critical point. Scattering intensities in a scattering vector (q) range from

Table 1. Characteristics of optical pressure cell at KUR-SANS.

Max. working pressure	20 MPa
Max. working temp.	100°C
Optical length	5-10 mm
Optical window size	ϕ=15 mm
Window materials	Al_2O_3(sapphire)
	ϕ25.5×131 mm

1.2×10^{-2} to 1.5×10^{-1} Å^{-1} were measured with a 5.6 Å-wavelength neutron beam. The q-range corresponds to the scale in a range from 5.2×10^{2} to 4.0×10^{1} Å in the real space.

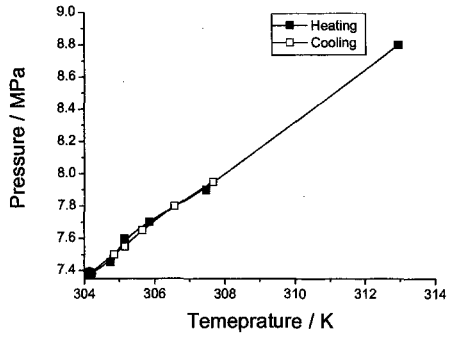

Fig. 2. SANS observation points in a phase diagram of CO_2 in the neighborhood of the critical point. Closed and open squares denote the observation points on heating and cooling processes, respectively. A big closed circle denotes the critical point.

Figure 2 shows SANS observation points in a phase diagram of carbon dioxide in the neighborhood of the critical point. The SANS experiments were performed on both of heating and cooling processes. The transmission of neutron for the CO_2-SCF with an optical length of 5 mm was 0.93, which was a good agreement with a calculated value, 0.94. The irradiation periods to accumulate enough scattering intensities were one and three hours in the observation near and far from the critical point, respectively.

Figure 3 shows temperature dependence of SANS profiles of the CO_2-SCF in the neighborhood of the critical point. Approaching the critical point, the scattering intensity in the low q-range gets more intense. This feature indicates that the dimension of density fluctuation becomes larger, which is one of the typical critical phenomena (critical opalescence).

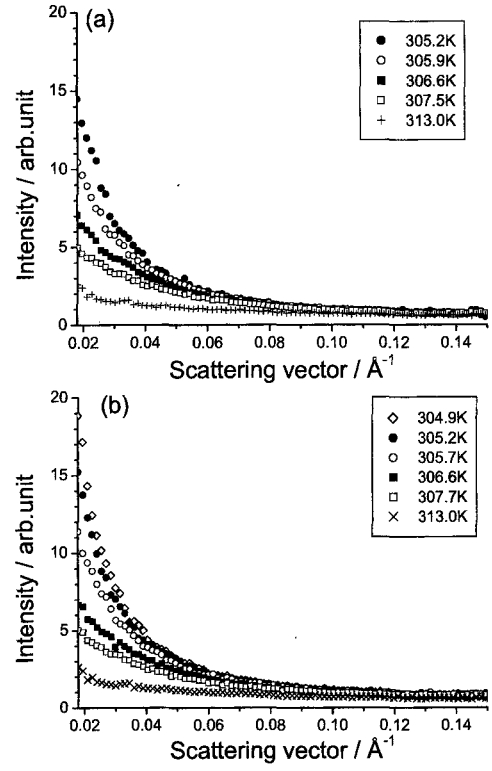

Fig. 3. SANS profiles of CO_2-SCF (a) on heating and (b) on cooling processes.

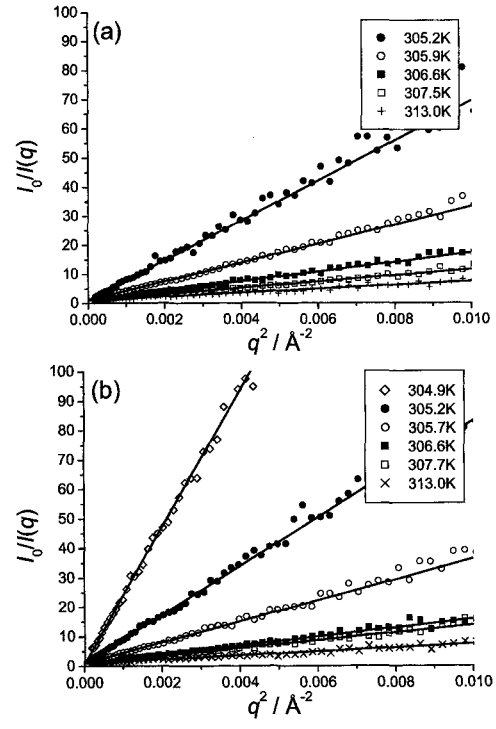

Fig. 4. Ornstein-Zernike plots of CO_2-SCF (a) on heating and (b) on cooling processes.

In order to estimate the dimension of the density fluctuation near the critical point, we adopt the Ornstein-Zernike function to fit the SANS intensity distribution following a classical theory[6]: the scattering intensity $I(q)$ is given by

$$I(q) = \frac{I_0}{1 + \xi^2 q^2}, \quad (1)$$

where ξ is a correlation length, which corresponds to the dimension of the density fluctuation.

As shown in Fig. 4, the scattering profiles are well reproduced by the Ornstein-Zernike function: solid lines show the results of the least square fitting with Equation (1). In the Ornstein-Zernike plot ($I_0/I(q)$ vs q^2), slope of a straight line corresponds to square of the correlation length (ξ^2). As can be seen from the figure, the correlation length also becomes longer, which means that the SCF becomes thermodynamically unstable with approaching to the critical point.

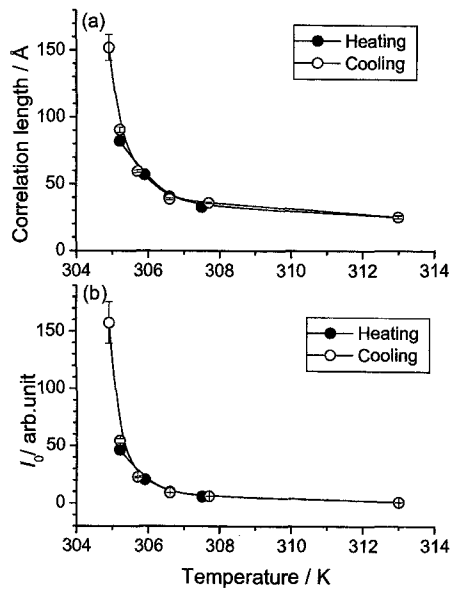

Fig. 5. Temperature dependence of (a) correlation length and (b) amplitude of density fluctuation.

The temperature dependences of the correlation length and the amplitude of density fluctuation are shown in Fig. 5. The amplitude of the density fluctuation I_0 is described as follows:

$$I_0 = \frac{< N^2 > - < N >^2}{< N >^2}, \quad (2)$$

where N denotes a number of SCF particles. As depicted in the figure, the correlation length and the amplitude show good agreement in both the heating and cooling processes, which is usually observed at the second order phase transition. The correlation length reaches ~150 Å at 304.7 K. Below this temperature (namely with approaching the critical point), the dimension of density fluctuation becomes an optical scale; visible lights cannot transmit through the SCF in that temperature range.

In summary, we have developed a CO_2-SCF system for an *in situ* SANS observation. In the preliminary experiments, the density fluctuation of CO_2-SCF has been revealed to induce a large contrast enough to observe the SANS intensity within three hours. In addition, the scattering intensities were well-explained by the Ornstein-Zernike picture. These results demonstrated that the newly developed SCF system is fully-functionated. Consequently, we may observe nano-structures of polymer solutions and/or gels saturated with CO_2-SCF by utilizing this system, which is now in progress.

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